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Measurements of Chemical Contaminants and Toxicological Effects in the Gully

Mesures des contaminants chimiques et des effets toxicologiques dans le Goulet

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ABSTRACT

This Research Document reviews knowledge of chemical contaminants and biological effects in the vicinity of the Gully Marine Protected Area (MPA) focusing on data collected since 1998. Spatial distributions of heavy metals in water and sediments of the Eastern Scotian Shelf are described as are distributions of hydrocarbons on Sable Bank. Knowledge of contaminants in biota is limited to some measurements of heavy metals and hydrocarbons in krill and persistent organic contaminants in seals and bottlenose whales. Concentrations of all of these contaminants are at or near background. Decreasing concentrations versus time on the Eastern Scotian Shelf are seen for hydrocarbons, lead, and zinc in water and persistent organic contaminants in seals. Acidity of shelf waters has been increasing. Within the Gully, bottlenose whales have shown increasing concentrations of 4,4'-DDE and trans-nonachlor. Even fewer measurements have been made of biological effects, these being restricted to measurements of sediment toxicity on Sable Bank and CYP 1A1 protein expression in bottlenose whales in the Gully. Some potential foci for additional research and monitoring are suggested.

RÉSUMÉ

Ce document de recherche examine les connaissances sur les contaminants chimiques et les effets biologiques à proximité de la Zone de protection marine du Goulet d'après les données recueillies depuis 1998. Les distributions spatiales des métaux lourds dans l'eau et les sédiments de la partie est du plateau néo-écossais sont décrites, tout comme les distributions des hydrocarbures sur le banc de l'île de Sable. Les connaissances sur les contaminants dans le biote se limitent à certaines mesures des métaux lourds et des hydrocarbures chez le krill et des contaminants organiques persistants chez les phoques et les baleines à bec. Les concentrations de tous ces contaminants sont égales ou proches des valeurs de fond. Les concentrations d'hydrocarbures, de plomb et de zinc dans l'eau et de contaminants organiques persistants chez les phoques sont à la baisse dans la partie est du plateau néo-écossais. L'acidité des eaux du plateau augmente. Dans le Goulet, les concentrations de 4,4'-DDE et de trans-nonachlore sont à la hausse chez les baleines à bec. Les effets biologiques ont fait l'objet d'encore moins de mesures, qui se limitent aux mesures de la toxicité des sédiments sur le banc de l'île de Sable et de l'expression de la protéine CYP1A1 chez les baleines à bec dans le Goulet. Ce document présente également des suggestions en matière de recherche et de surveillance.

HISTORY OF CONTAMINANT STUDIES IN GULLY AREA

Knowledge of chemical distributions and their relationships to both biological and physical oceanographic processes were reviewed in the Gully Science Review (Harrison and Fenton, 1998). This document included chapters on the geological setting, physical, chemical and biological oceanography, fish and fisheries, seabirds, and marine mammals, and can be referred to for background information on any of these topics. The chemistry focus in this review was on nutrients, oxygen, and chlorophyll, not contaminants. The chapter on chemical oceanography includes a statement that says no contaminant studies have been conducted in the Gully, but did make reference to a number of studies in the adjacent Sable and Banquereau Bank areas.

Several documents reviewing and assessing knowledge of contaminants and effects on broader areas of the Eastern Scotian Shelf were prepared at about the same time as the Gully Science Review. These include a review of contaminants on the Scotian Shelf by Stewart and White (2001, reviews knowledge up to 1995) and several reports related to the Sable Offshore Energy Project (SOEP) that review knowledge about environmental conditions, including contaminant concentrations and effects in the Sable project area (SOEP, 1996), as well as providing some new background survey data (SOEP, 1999). A large number of studies on potential effects of offshore oil and gas development, some of which include data from the Sable area, have been conducted by scientists in the oil industry, universities, and government labs. The proceedings of an environmental effects workshop at the Bedford Institute of Oceanography (BIO) (Gordon et al., 2000) and the monograph Offshore Oil and Gas Environmental Effects Monitoring (Armsworthy et al., 2005) consolidate the results of some of this research. The Eastern Scotian Shelf Ecosystem Workshop (O'Boyle, 2000) reviewed what was known about a broad range of indicators of ecosystem health on the eastern shelf, with a focus on temporal trends in the data. Temporal trends for a limited number of contaminant measures including oil, PCBs, DDTs, dissolved Cu, and metals in sediments were identified in this review. Frank et al. (2005) have continued this investigation of environmental change on the Eastern Scotian Shelf (DFO, 2003). The environmental assessment documents prepared for the Deep Panuke project (EnCana, 2002) represent a more recent review of environmental knowledge for the Sable Bank area, including some additional data on contaminants in sediments. These and all other available data were combined to prepare maps of the spatial distributions of several heavy metals in water and sediments for the Scotian Shelf (Breeze and Horsman, 2005). These maps show both the concentrations of the metals and their relationships to water and sediment quality guidelines.

Since 1997, several projects at BIO have focused specifically on the Gully. The Atlantic Zonal Monitoring Program (AZMP) added stations in the Gully to the twice annual surveys of physical, chemical, and biological oceanographic conditions on the Scotian Shelf. This expansion of the AZMP included periodic measurements of dissolved heavy metals, as well as collection of krill samples for contaminant analysis. The Don Gordon-led Gully research project from 1999 to 2001 (Gordon and Fenton, 2002) included extensive measurements of nutrients, but no contaminant measurements. The nutrient results from this project and other data for the eastern shelf have been synthesised (Strain and Yeats, 2005). More recently (2006/2007) projects funded by the Oceans Action Plan, DFO Science A-base, and the Panel for Energy Research and Development (PERD) have resumed measurements of environmental conditions, including collections and analysis of sediment and biota samples for contaminants. PERD funded cruises in 2006 and 2007, collected sediment samples on the western edge of the Gully to aid in sample collection for SOEP Environmental Effects Monitoring (EEM) program. The Biodiversity cruise in 2007 also collected sediment cores in the Gully using the remotely operated vehicle, ROPOS. Finally, the BIO BIOCHEM database has been used to archive chemical and biological data collected by scientists from BIO and elsewhere for waters off the east coast of Canada,

including the Scotian Shelf. It has extensive holding of data for parameters that include oxygen, nutrients, chlorophyll, carbonate, pH, and heavy metals extending in time from the 1930s to the present. This database provides a resource for the investigation of carbon dioxide, a contaminant whose environmental effects for an area like the Gully may not have been adequately considered.

The cetacean science group at Dalhousie University led by H. Whitehead has been studying whales in the Gully for many years. Their investigations have included measurements of floating plastic debris (Dufault and Whitehead, 1994; Scarfe, unpub. manusc.) and persistent organic contaminants and multifunction oxydase (CYP1A1) enzyme induction and other potential biological effects observations in northern bottlenose whales (Hooker et al., 2008; Mitchell, 2008). The SOEP EEM program has also conducted on-going measurements of Ba, Hg, total hydrocarbons, and amphipod mortality on sediment samples from the Gully (SOEP, 2008).

CONTAMINANT SOURCES

Any assessment of the impacts of contaminants on the marine environment should start with a consideration of the sources of the contaminants. For the Gully, these sources will include dry and wet atmospheric precipitation, transport of riverborne contaminants via coastal currents, and transport of contaminants from oceanic waters via shelf edge water exchange, as well as more localized sources, including the offshore oil and gas developments on Sable Bank, shipping, and, possibly, dumping of munitions and other wastes. Atmospheric deposition will bring contaminants from nearby sources (gas platform flares and ship stacks), more distant land based activities (smoke stacks, emissions from vehicles, dust formation, evaporation from land or vegetation, etc.), as well as evaporation and particle generation from the sea surface. This route will be most important for volatile contaminants (volatile organic compounds, mercury) and non-volatile contaminants (e.g., lead) that are emitted from stacks. For the Gully, the main source for riverborne contaminants will be freshwater discharge into the Gulf of St. Lawrence, and subsequent transport out of the Gulf in surface currents that flow to the southwest across the Scotian Shelf and around the shelf break. For offshore waters, this river input will be a source for more water soluble heavy metals and organic contaminants, while more lipophilic and particle reactive chemicals will bind to particles and be preferentially deposited in more inshore sediments. More oceanic water flows into the Gully at depth. This source will be most important for contaminants that remain in solution in seawater and have long residence times. The obvious example for a contaminant that will have a dominantly offshore source is cadmium. The offshore oil and gas development could be an important source for specific contaminants that are discharged to the water in drilling wastes (e.g., barium) or with produced water and other production wastes. The SOEP environmental Impact Statement (EIS) (SOEP, 1996) provides data for an assessment of the maximum potential discharges in produced water and for several contaminants including lead and zinc, these could be quite large. Results for actual measurements of metals and hydrocarbons in produced water discharged from the SOEP platforms included in several of the more recent EEM program reports (SOEP, 2006, 2007, 2008) show that the concentrations of these metals in the discharges measured to date are quite variable, but considerably less than the maximum concentrations predicted in the EIS. We have no information on inputs of contaminants to the Gully from shipping or other sources.

We have made estimates using the data we could locate for the magnitudes of the transport vectors and the contaminant concentrations for 3 metals as shown in Table 1 (the produced water estimates are based on the maximum concentrations listed in the SOEP EIS (SOEP, 1996)). The uncertainty on any of the transport estimates is high, but the results do give some indication of the relative importance of the various sources.

As we move to the smaller scale of the Gully, the relative importance of these sources will change. The offshore input to the shelf remains virtually the same, because most of this input is into the Gully, whereas the input from the Gulf of St. Lawrence to the Scotian Shelf will be spread out over a large area, and only a fraction will get to the Gully. Other inputs and transport mechanisms may also gain (or lose) importance. For example, the transport of near bottom particulates and resuspended sediment material from Sable Bank to the Gully via the small canyons on the western side of the Gully may turn out to be an important transport mechanism for contaminants from Sable Bank.

TEMPORAL TRENDS IN CONTAMINANTS

The first studies from BIO that generated data on contaminants on the Eastern Scotian Shelf that gave an indication of temporal trends were focused on oil in water, chlorinated organics in seals, and heavy metals in water. The study of dissolved and dispersed oil in water in the 1970s was conducted to generate data that would be useful in international efforts that were being made to reduce discharges of oil from ships. The data that reflects snapshots of concentrations due to fluorescing compounds obtained over time (Figure 1) shows a lot of scatter, and perhaps some indication of decreasing trend. When these results were presented at the Eastern Scotian Shelf Ecosystem Workshop (O'Boyle, 2000), participants from the Canadian Wildlife Service pointed out that observations of oil on birds did not show a decreasing trend. The study of various chlorinated organics in seals from Sable Island (Addison et al., 1998) also shows decreasing concentrations with time (Figure 2) that indicate a decrease in atmospheric transport of these contaminants to the eastern shelf, but a comparison of concentrations of the same persistent organic contaminants in bottlenose whale samples collected in 1996/1997 and 2002/2003 indicated an increase in concentrations of 4,4'-DDE and trans-nonachlor (Hooker et al., 2008). Higher concentrations were found in males than females. The on-going study of metals in water (Figure 3) shows decreasing trends with time for several metals. For lead, decreases are associated with reduction in anthropogenic releases of lead to the atmosphere (elimination of lead in gasoline being a major contributor to this decrease). For metals such as zinc, decreases in industrial discharges to rivers are more likely to be responsible for the observed trends, but for copper, no decrease is observed. The overall picture is one of decreasing concentrations in water for 2 'traditional' heavy metal contaminants whose inputs have been regulated in one way or another, but a less consistent picture for organic contamination levels in biota. The seal data indicate a decrease in organochlorine concentrations from 1974 to 1994, but the bottlenose whale data indicate increases in concentrations for 2 of these contaminants between 1996/1997 and 2002/2003. In comparison to these results, in the Baltic Sea, the levels of pp'-DDE and pp'-DDD detected in whole fish decreased between 1995 and 2006; while those of p,p'-DDT did not exhibit an obvious trend (Szlinder-Richert et al., 2008). As well, levels of PCB and DDT in blubber of ringed seals from Central Western Greenland also decreased between 1994 and 2006 (Vorkamp et al., 2008). In another review of Arctic contaminants, it was pointed out that while legacy contaminants decreased between the late 1970s and late 1990s, additional data are needed to assess trends for current use chemicals that have potential for toxicity (Braune et al., 2005).

The Dalhousie whale research group has also measured concentrations of floating debris (mostly plastics) in the Gully. An initial survey was conducted in 1990 (Dufault and Whitehead, 1994), and a second report looked at differences between the 1990, 1996/1997 and 1999 surveys (Scarfe, unpub. manusc.). The observed quantities of large debris (Table 2) decreased from 1990 to 1999, but quantities of smaller debris collected with plankton nets were similar in all 3 surveys. Results of some measurements conducted on continuous plankton recorder

(CPR) samples collected in European waters indicate that concentrations of microscopic plastic fragments and fibres have been increasing in line with general increases in global production of synthetic fibres (Thompson et al., 2004). Plastic fibre measurements have not been made on Eastern Scotian Shelf CPR samples.

Another contaminant whose concentration is not decreasing with time is carbon dioxide. Dissolution of CO_2 in the ocean generates carbonic acid, which disassociates into hydrogen, bicarbonate, and carbonate ions. The well known global increases in atmospheric and oceanic CO_2 are clearly evident in the changes in pH (negative logarithm of the hydrogen ion concentration) on the Scotian Shelf (Figure 4). Figure 4 provides a very simple picture of the decreases in pH with time. A more rigorous multivariate analysis of the data shows that pH varies with time, depth, location on the shelf, and season. The trend with time after accounting for these other dependencies is highly significant and corresponds to a decrease of 0.002 pH units per year. Increases in CO_2 could stimulate more primary productivity, but increases in H^+ (decreases in pH) will negatively affect the ability of carbonate shell forming organism to form and maintain their shells.

SPATIAL DISTRIBUTIONS OF CONTAMINANTS

All available data on several heavy metals in Scotian Shelf sediments were combined in 2005 to produce maps of both metal concentrations and relationships to sediment quality guidelines. Data sources included contaminant databases in both Department of Fisheries and Oceans (DFO) and Natural Resources Canada (NRCan), as well as reports from SOEP (SOEP, 1999) and deep Panuke (EnCana, 2002). The sediment quality map for lead shown in Figure 5 is one of the contaminant maps produced for the Scotian Shelf atlas of human activities (Breeze and Horsman, 2005). We also have maps for cadmium, chromium, copper, and zinc, and others could be generated. Figure 5 shows low concentrations of lead and a distribution that mostly reflects the grain size of the sediments with lower concentrations on the banks compared to the basins. Almost all the samples are at 'background' concentrations and none are above the CCME threshold effects level sediment quality guideline. Similar maps can also be prepared for dissolved copper and several other heavy metals at various depth intervals on the shelf. In order to make these dissolved metal maps, we need to establish the correlation between the metal concentrations and some physical or chemical oceanographic parameter like temperature, salinity, nitrate, silicate, or oxygen. We can then use the optimally estimated distribution field for the physical or chemical oceanographic parameter and the regression equation(s) to generate the distribution for the metal. The distribution of dissolved copper at 0 m depth (Figure 6) quite clearly shows the spreading of high copper concentrations that originate mostly in the Gulf of St. Lawrence rivers across the Scotian Shelf to the Gully.

In the past decade, some measurements have been made of contaminant concentrations in the Gully (Figure 7). The initial baseline survey for the SOEP (SOEP, 1999) included measurements of suspended particulate matter and particulate barium, as well as extractable petroleum hydrocarbons in benthic boundary layer samples at 5 sites at the edge of Sable Bank adjacent to the Gully. Suspended particulate matter (SPM) concentrations were not abnormal, and particulate Ba and hydrocarbons were all below detections limits for the methods used. Sediments at these sites were very coarse with low concentrations of heavy metals, as would be expected for such coarse sediments and no detectable concentrations of hydrocarbons. Measurements of Ba, Hg, and total hydrocarbons in sediments from these sites have been continued in the SOEP EEM program. We first collected dissolved metal samples in the Gully in 1997, with additional samples collected subsequently on several of the AZMP cruises. None of

the concentrations measured were significantly different from those measured on the Louisbourg section.

In 2006, sediment samples for hydrocarbon and metal analysis were collected on 4 different 'cruises of opportunity'. Four sediment grab samples were collected from 84 to 100 m depth on the eastern edge of Sable Bank, from the heads of small canyons feeding into the Gully on the Spring 2006, AZMP cruise. Samples from 11 sites on the eastern edge of Sable Bank were collected, using a hydraulically damped slo-corer during PERD funded Produced Water cruises lead by DFO COOGER and the Particle Dynamics Lab, BIO, in 2006 (7 sites) and 2007 (4 sites). Four of the 2006 sites coincided with the AZMP grab stations. Results of Ba, Hg, and total hydrocarbon measurements from the 2007 sites are included in the 2007 SOEP EEM report (SOEP, 2008). Six additional cores from greater depths in the Gully were collected during the 2007 Biodiversity cruise of Dr. E. Kenchington using the ROV, ROPOS.

Results for hydrocarbon analyses at BIO of sediment grab samples collected from the 4 feeder canyons sites in 2006, using more sensitive techniques than those used in most of the SOEP EEM program are presented in Figure 8 and Table 3. Aromatic hydrocarbons were not detected in these samples, but the samples do contain total alkanes (C_{10}-C_{35}) ranging in concentrations from 966 to 6486 $ng.g^{-1}$ (dry wt.). In the 2 years in which they employed sufficiently sensitive techniques in their EEM program, SOEP reported similar (560 to 5450 ng/g) concentrations for their Gully stations (SOEP, 2008). These concentrations and fingerprints are consistent with observations of hydrocarbon concentrations in mostly uncontaminated sandy shelf sediments elsewhere (e.g., Gogou et al., 2000, and references therein). As described in the paragraph below, metal concentrations in these sediments collected at similar locations in 2006 and 2007 are also at background concentrations.

There are many sources for hydrocarbons detected in the marine environment, including industrial effluents, sewage, river drainage, loading and dumping in shipping operations, and offshore oil and gas production (Nishigima et al., 2001). Hydrocarbons with predominantly odd carbon number *n*-alkanes and pristane are preferentially produced by marine organisms and plants (Nishigima et al., 2001). Sediments that are not contaminated with petroleum hydrocarbons have pristane/phytane ratios are >1, usually between 3 and 5 (Steinhauer and Boehm, 1992). Thus, the ratio of odd/even carbon number alkanes, pristane/phytane ratios, and the presence of complex unresolved mixtures in chromatograms can be used to distinguish between natural and anthropogenic sources (Nishigima et al., 2001). In our samples, the pristane to phytane ratios ranged from 0.93 to 1.08, suggesting anthropogenic sources for the hydrocarbons detected within the sediments. If we look at the overall distribution of odd/even alkanes (0.91-1.21), it reveals no real dominance of odd carbon number alkanes again suggesting the potential contribution of petrogenic hydrocarbons to the sediments (Volkman et al., 1992). The dominance of odd *n*-alkanes with low molecular weight ($<C_{24}$) would suggest that the origin of hydrocarbons are from biogenic sources that are mostly marine phytoplankton, while dominance of those with high molecular weight ($\geq C_{24}$) indicates that the hydrocarbon input to the sediment may be from higher plants (Zanardi et al.. 1999). In our particular case, ratios of odd/even for $<C_{24}$ are in the range of 0.91-1.08. The odd/even $\geq C_{24}$ are in the range of 1.18-1.98 for 3 samples with detectable high carbon number alkanes. The higher odd/even for $\geq C_{24}$ suggests some hydrocarbon input linked to natural production from higher plants. Overall, the results suggest both a biogenic and anthropogenic source of hydrocarbons dominated by the alkane fraction.

Results of metal analyses on 7 sediment cores collected by DFO in 2006, and 10 in 2007, together with Ba and Hg measurements on Gully sediments by SOEP (SOEP, 2008), provide the most extensive dataset for contaminants in the Gully. Metals are naturally occurring

components of the sediments whose concentrations generally decrease with increasing grain-size, and any assessment of anthropogenic inputs must account for the natural variability. As illustrated by the Ba versus Li plot for sediments on Sable Bank (Figure 7.4 in SOEP, 2008), this is generally done by geochemical normalization using an element such as Al whose concentrations reflect only mineralogical and grain-size variability. When plotted against Al (or Li), the concentrations of Cr, Cu, Fe, V, and Zn all show patterns that are indicative of natural concentrations. The concentrations for the Sable Bank stations are lower than those for the deeper ROPOS stations, but all follow linear relationships with Al that are consistent with earlier observations for the Scotian Shelf. The pattern for Ba is more complicated, because the Ba versus Al relationships for bank and slope sediments are different and only well constrained for the bank sediments. Very few deviations from natural distributions are evident for Sable Bank samples from within the Gully MPA. Two of the samples from the 2006 Sable Bank sampling exceed those predicted from the Ba versus Al relationship for Bank sediments (Figure 9). No deviations were seen in the 2007 sampling nor in the SOEP EEM program sediment sampling (SOEP, 2008), but benthic boundary layer suspended matter has on occasion shown elevated concentrations of Ba (SOEP, 2000). Barium is a well known contaminant in drilling wastes and produced waters and larger deviations from the expected Ba versus Al relationship are seen more frequently in sediments within a kilometer or so of drill sites. Remobilization of Ba initially deposited in sediment close to drilling rigs by storms has been observed and produced water Ba would generate finer-grained particles that would not settle as quickly as drilling mud Ba. So, transport of Ba greater distances from well sites is not out of the question. However, we only see excess Ba in 2 samples from 1 of 20 sampling sites on the eastern end of Sable Bank. Identification of excess Ba in finer sediments from the deeper parts of the Gully will require a better understanding of the Ba grain-size relationships for basin/slope sediments. Lead is the only other element that shows any deviations from the expected metal versus Al relationships. In this case (Figure 10), the concentrations for 9 Gully samples from the finer-grained sediments collected deeper in the Gully exceed those predicted from the natural Pb versus Al relationship. All of these samples are from the top portions of sediment cores from 3 stations located along the main axis of the Gully. The transport pathway for this Pb input is not clear at present, nor is its potential importance for environmental quality in the Gully. Lead can be at elevated concentrations in produced waters, but so can Cr, V, and Zn, and these elements do not show excess concentrations in the Gully sediments.

Fewer measurements have been made of contaminants in Gully biota. The SOEP baseline survey that was conducted at the beginning of their Environmental Monitoring Program (SOEP, 1999) includes alkane and metal measurements for 3 groups of scallops from a reference site on Banquero, a site on Sable Bank near the Venture platform (near the western edge of the Gully), and a site near the Thebaud platform. The results from all 3 sites are similar. We collected a small number of krill (*Meganyctiphanes norvegica*) samples in the Gully on AZMP cruises between 2004 and 2006, and preserved them for metal and hydrocarbon analysis. Krill turned out to be very hard to find, so the sample set was smaller than originally planned. Metal concentrations have been measured, and initial organic contaminant measurements have shown that the samples contain pristane but no other detectable alkanes and very low (few ng/g) concentrations of alkylated and parental PAHs. Cr, Cu, Pb, Zn, and, more notably, Fe and Sn concentrations (Table 4) may be higher in the sample from Emerald Basin than in those from the Gully; but without more replication, we cannot test the significance of any differences. Measurements of Cd, Cu, Zn, and Pb concentrations from *M. norvegica* in the Barents (Zauke and Schmalenbach, 2006) and Greenland (Riterhoff and Zauke, 1997) seas give results that are very similar to our Gully results, suggesting that the Gully is a rather clean area for these metallic contaminants. On the other hand, Hooker et al. (2008) have shown that concentrations of PCBs and DDTs are higher in blubber of northern bottlenose whales from the Gully than in those collected off northern Labrador. They discuss the difficulty in interpreting results of

blubber biopsies from whales and the confounding effects that variables such as sex, age, or size will have on the results. Lipid content was also surprisingly low and variable (38-63%). All these factors, plus the observations of non-detectable concentrations of analytes in half of the samples, make comparisons difficult.

BIOLOGICAL EFFECTS

Much research has been conducted on the toxicity of chemical contaminants to marine organisms, and all of the contaminants discussed in this research document have been shown to cause toxicity. Finding actual field measurements of biological effects; however, is more difficult, and very few toxicological measurements have been made in the Gully. The Hooker et al. (2008) study of organic contaminants in bottlenose whales included measurements of CYP1A1 protein expression in the whales, and their results showed increased activity in 2003 samples that could perhaps be associated with spills of kerosene and streamer fluids. They also observed that CYP1A1 activity was lower in whales from the Gully than in whales from northern Labrador, opposite to the trend in persistent organic contaminant concentrations. Mitchell (2008) examined changes in the incidence of skin markings on photographs of bottlenose whales from the Gully. She found a substantial and statistically significant increase in the incidence of non-circular patches in photographs following 2004. The sample size was small as this was a preliminary and incidental study. These marks are similar to those considered to be disease related in bottlenose dolphins.

Sediment toxicity data from stations at the edge of the Gully MPA on the eastern extremity of Sable Bank have been collected as part of the SOEP EEM program. In the initial (1998) survey, one (echinoid fertilization assay) of 3 standard Environment Canada toxicity tests employed (the other 2 were Microtox luminescent bacteria assays and amphipod survival assays) showed toxicity in 3 of 5 Gully samples (the other 2 tests showed no toxicity), but the toxicity did not appear to be associated with any SOEP related chemical contamination (SOEP, 1999). Results of tests conducted in 1999 were similar (SOEP, 2000), but more recent SOEP EEM studies (SOEP, 2001, 2002, 2006, 2007, 2008) have focused on amphipod survival, and no acute toxicity was reported.

CONCLUSIONS

Most of the research on contaminants in the Gully and its immediate vicinity has focused on contaminant pathways and accumulation in biota. In different studies of temporal trends, decreasing concentrations have been observed for Pb and Zn (and some other heavy metals) in water and PCBs and DDTs in seals, but increasing concentrations of 2 organochlorines are seen in bottlenose whales. Continuation of the sporadic surveys of metals in the water, resurrection of the organic contaminants in seals, and additional measurements in whales would provide on-going data on trends in contaminant exposure and bioaccumulation in the Gully.

Recent measurements of individual alkanes in sediments from the eastern edge of Sable Bank give some indication of sources for the hydrocarbons observed in these sediments. Since only 4 samples were studied, it is difficult to get a clear indication of the dominant hydrocarbon source. While not conclusive, the initial survey gives an indication that an anthropogenic source is likely. Collection and analysis of additional sediments from more locations would provide a clearer picture of both the concentrations of hydrocarbons and their sources.

Most metallic contaminants from land based sources will eventually be deposited in fine grained sediments. This is the process for accumulation of metals in Emerald and other shelf basins, and will also be important for the Gully, especially the inner part. The Gully will also be a potential trap for metals transported from offshore and discharged to and mobilized by activities on the outer banks. Based on sediment sampling to date, extent of contamination appears to be small – we observe some elevated concentrations of Pb, and cannot properly assess the situation for Ba. Sediments on the eastern end of Sable Bank have been much better sampled than the deeper areas, where contaminants may be accumulating. A more extensive sampling of metals and other contaminants in finer grained sediments from the Gully MPA, as well as sampling from nearby basins for comparison purposes would be required to delineate the extent of any contamination and identify accumulation areas.

Measurements of contaminants in biota and biological effects are very limited and somewhat contradictory. Very little can be concluded about accumulation of contaminants in biota or their potential for causing effects, without additional sampling that fills in some of the gaps in analytes targeted, distributions of contaminants within the organisms, and trophic levels of the biota. For example, crabs have been sampled in many areas surrounding the Gully where they are commercially fished. Since crabs feed on organisms living in the sediments, they would integrate the levels of contaminants present and bioavailable in that habitat, where lipophilic contaminants would be deposited. Organs representative of long-term and short-term exposure would provide a good view of the state of the ecosystem that the animals are exposed to and their ability to act as a vector for contaminants within the food chain. A geographical comparison would also help interpret the origin of the contamination and place the results in perspective. A recent publication on biomarkers in crabs (Morales-Caselles et al., 2008) provides some information on potential approaches to examine the health status of these animals.

Additional measurements in whales would provide on-going data on bioaccumulating contaminants in blubber of mammals inhabiting the Gully. Analytes in any biomonitoring program should include current use chemicals of concern, not just legacy contaminants, as well as effects biomarkers for comparison of health status at various sites.

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Table 1. Contaminant inputs to the eastern Scotian Shelf.

	Cu (tonnes/yr)	Pb (tonnes/yr)	Zn (tonnes/yr)
Gulf of St. Lawrence	4390	258	7750
Offshore to Shelf	279	37	409
Rainfall	90	90	270
NS rivers	32	30	97
'sewage'	5	3	11
Produced water	<1	23	157

Table 2. Observations of floating debris in the Gully (based on Scarfe, unpub. manusc.).

	1990	1996/1997	1999	Statistical significance of trend
Large debris (visual observations, items/km^2)	105.4	36.1	20.3	P=0.000
Small debris (neuston nets, mg/m^2)	0.012	0.145	0.025	P=0.319

Table 3. Evaluation of hydrocarbon sources in Gully sediments.

	Sed-2	Sed-3	Sed-4	Sed-5
latitude	44.0311	44.0472	44.0657	44.0739
longitude	59.2060	59.2192	59.2289	59.2516
Pristane/Phytane ratios	1.05	0.93	1.08	1.01
Σodd C# (ng/g dry wt.)	813	3263	1561	318
Σeven C# (ng/g dry wt.)	74	2870	1395	349
odd/even ratios	1.21	1.14	1.12	0.91
Σodd $<C_{24}$ (ng/g dry wt.)	476	1284	853	318
Σeven $<C_{24}$ (ng/g dry wt.)	504	1191	867	349
odd/even $<C_{24}$ ratios	0.95	1.08	0.98	0.91
Σodd $>C_{24}$ (ng/g dry wt.)	337	1979	708	
Σeven $\geq C_{24}$ (ng/g dry wt.)	170	1679	386	
odd/even$\geq C_{24}$ ratios	1.98	1.18	1.83	
Σalkanes ($ng.g^{-1}$ dry wt.)	1768	6486	3239	966

Table 4. Metal analysis of krill (μg/g, dry).

	Gully	Gully	Emerald Basin
	2004 (n=3)	2006 (n=3)	2006 (n=1)
Al	42±16	38±31	34
As	6.2±4.8	11.4±5.6	11.0
Cd	0.21±0.15	0.34±0.21	0.18
Cr	0.8±0.3	0.6	1.4
Cu	31±21	28±9	68
Fe	45±5	55±26	246
Pb	0.14±0.07	0.15±0.09	0.33
Ni	0.5±0.2	0.5±0.1	1.4
Sn	0.15±0.18	0.17±0.17	5.9
Zn	48±5	51±7	82

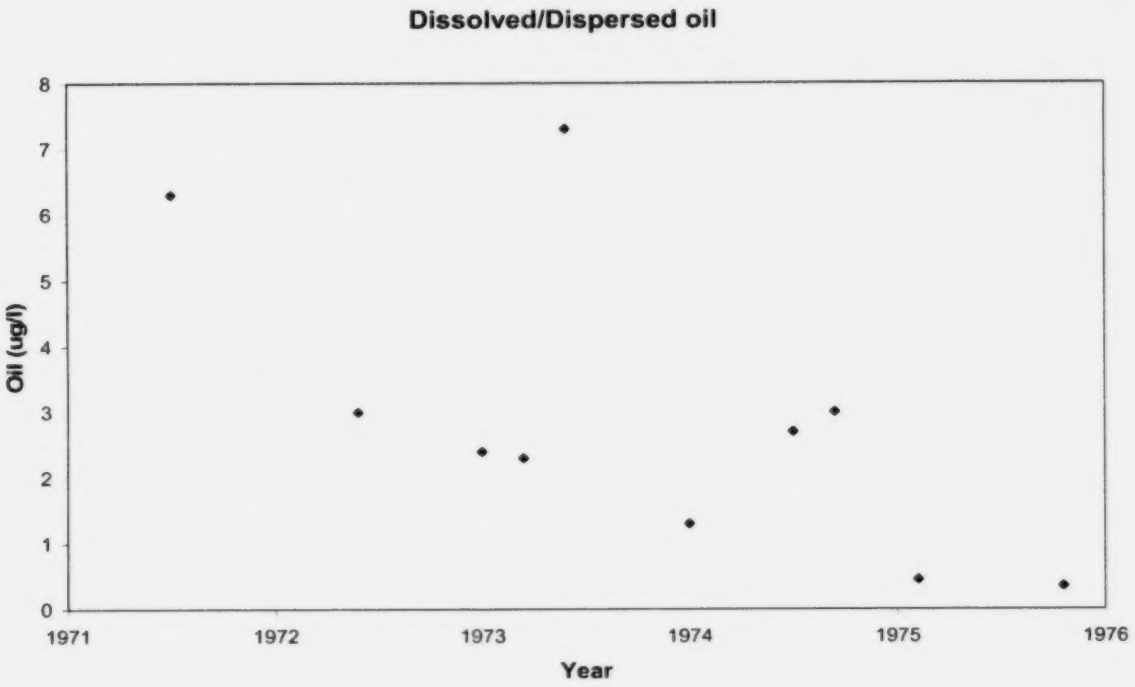

Figure 1. Dissolved and dispersed oil on Eastern Scotian Shelf.

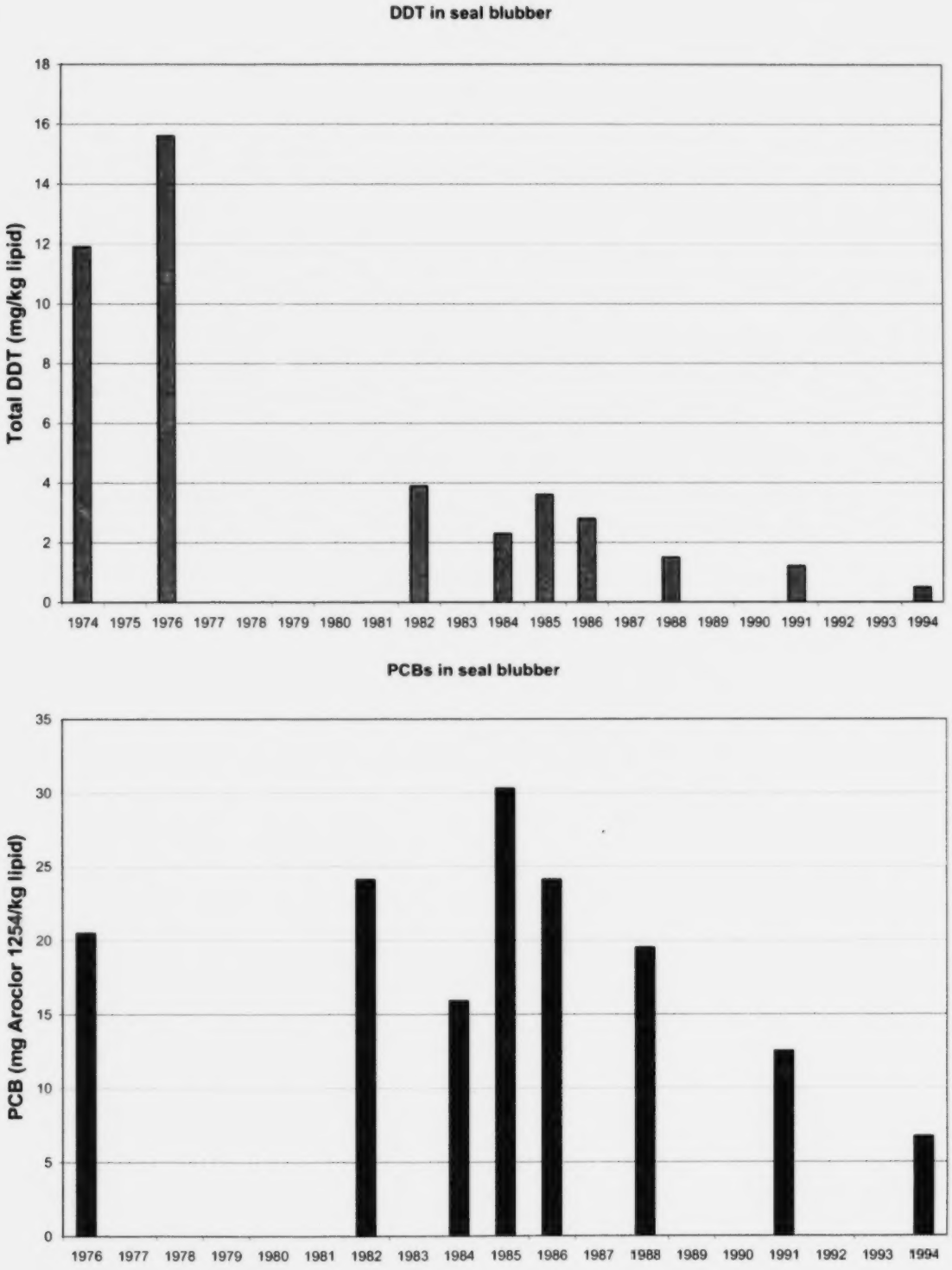

Figure 2. Organochlorine compounds in Sable Island seals (based on Addison et al., 1998).

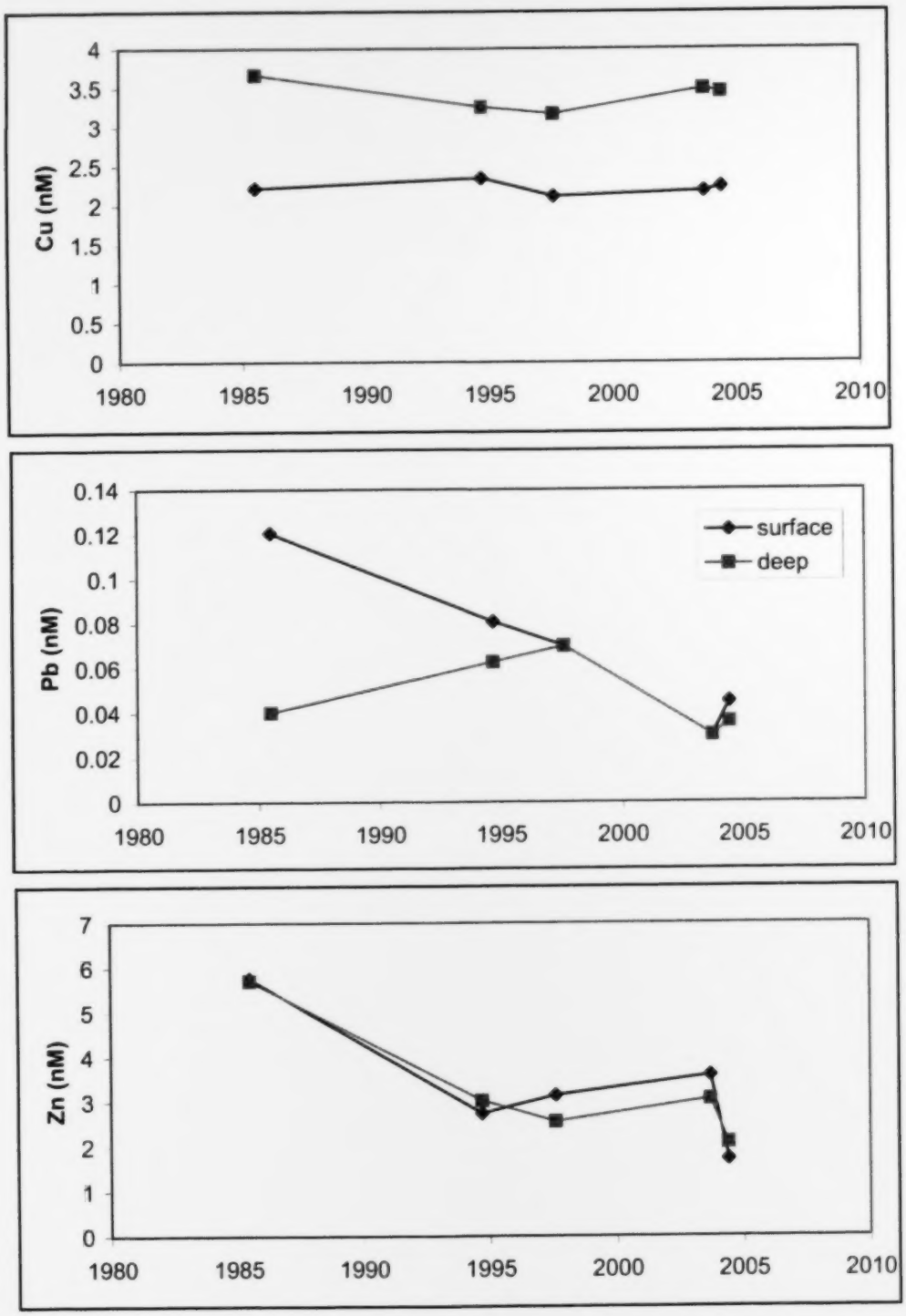

Figure 3. Temporal trends in heavy metal concentrations on the Eastern Scotian Shelf.

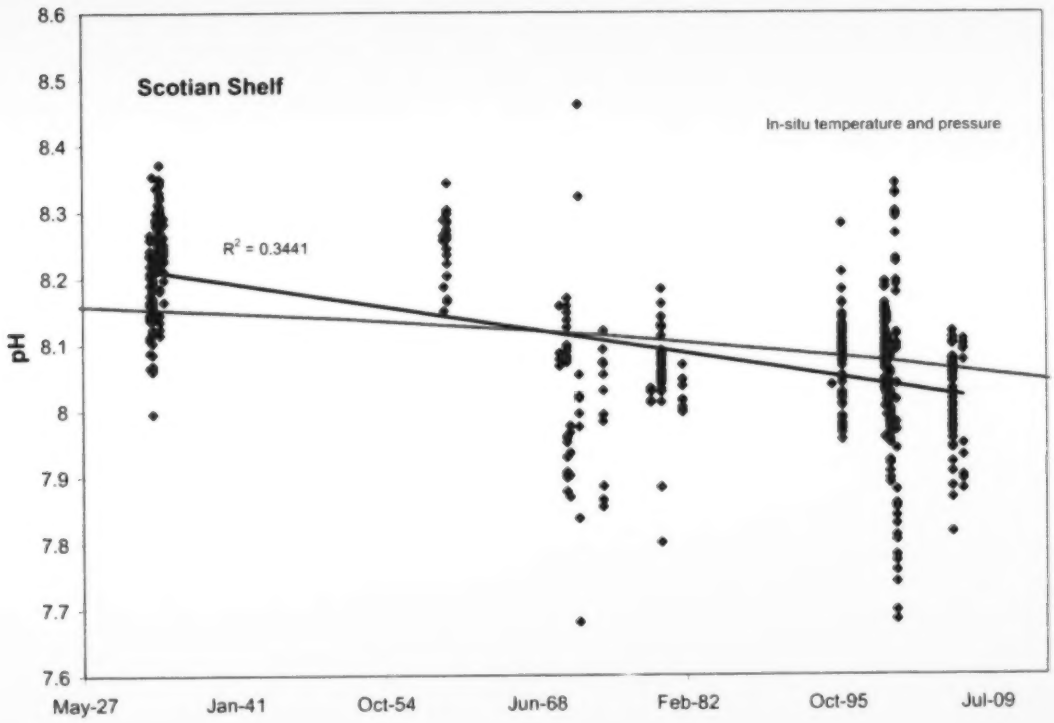

Figure 4. pH trends on the Scotian Shelf. Curved red line shows the global average trend in ocean pH.

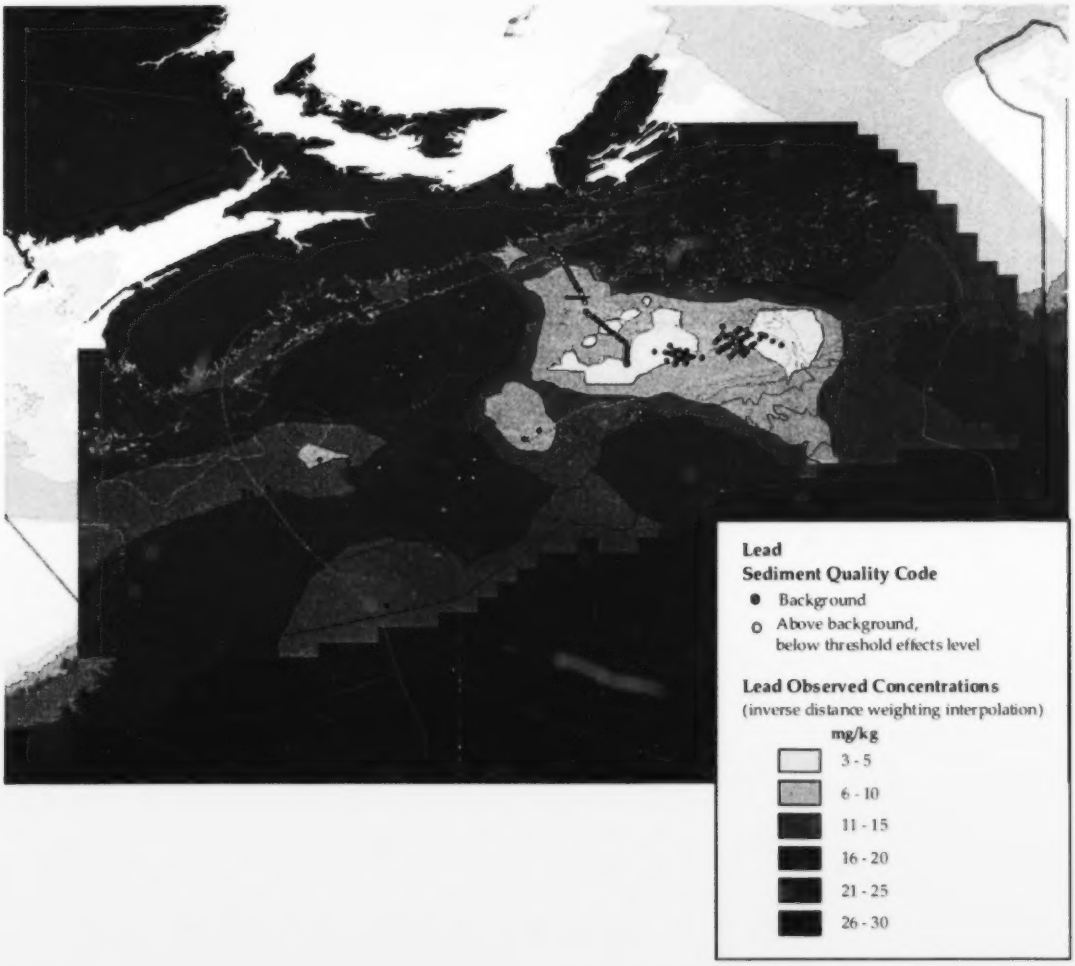

Figure 5. Distribution of total lead in sediments (from Breeze and Horsman, 2005).

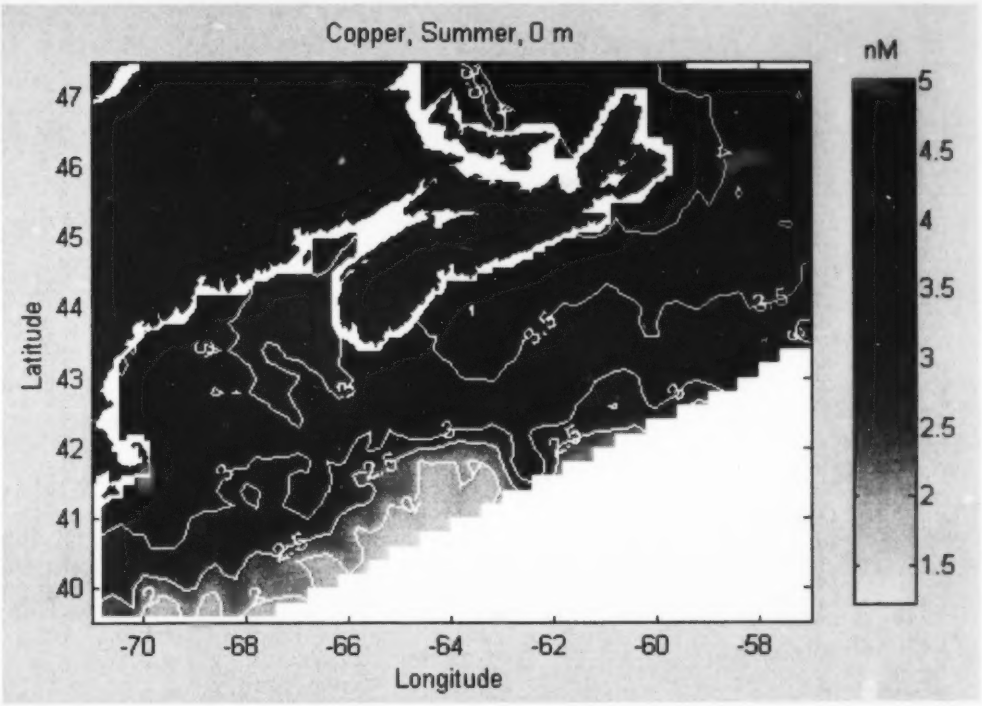

Figure 6. Optimally estimated summertime surface dissolved copper distribution.

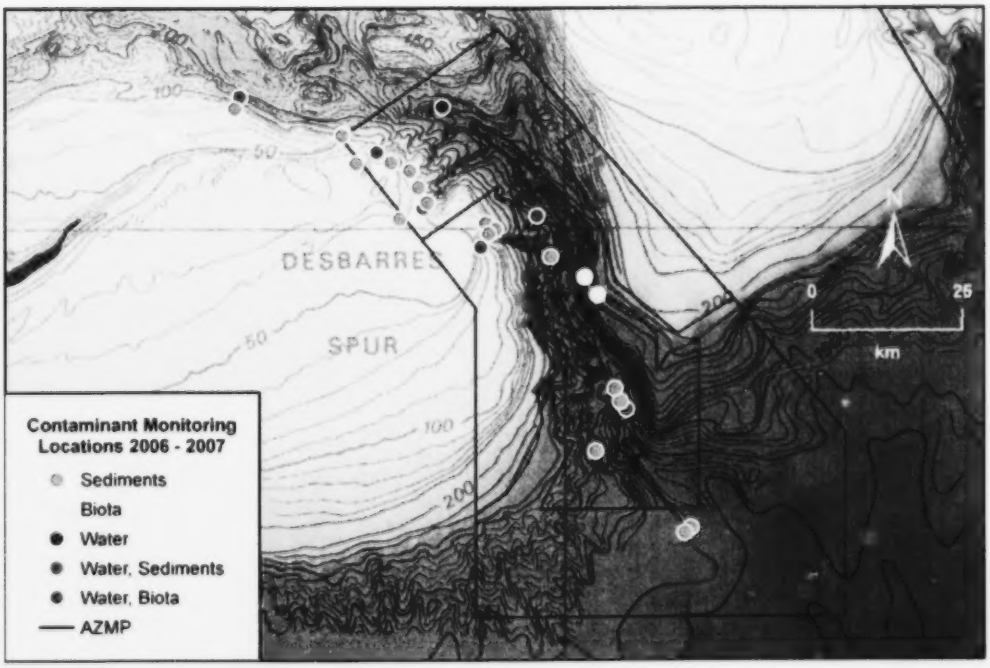

Figure 7. Map showing contaminant sampling locations in the Gully.

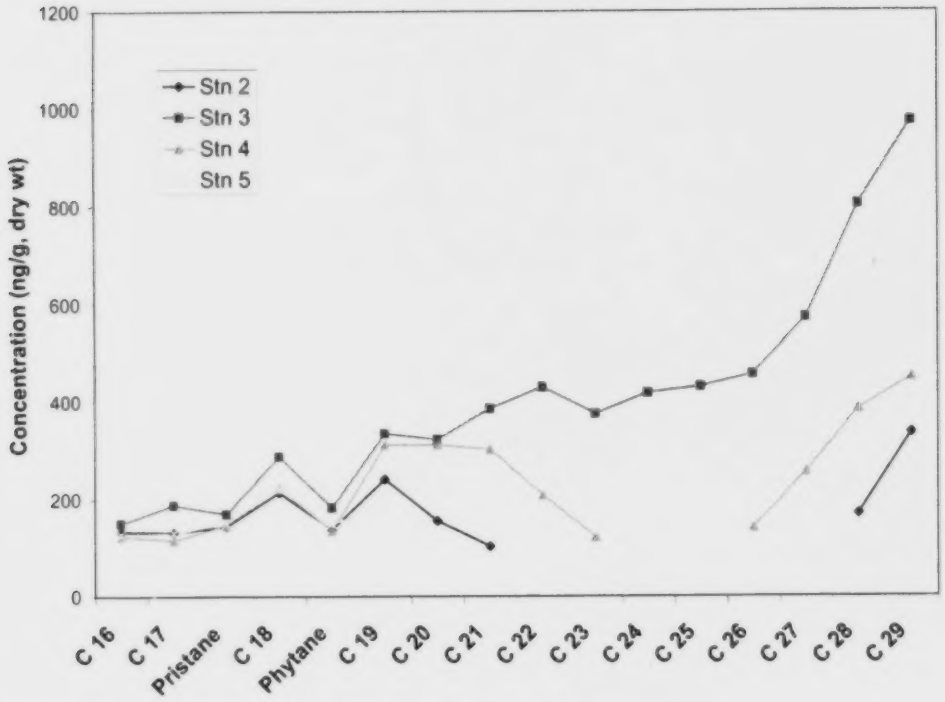

Figure 8. Hydrocarbon concentrations in Gully sediments.

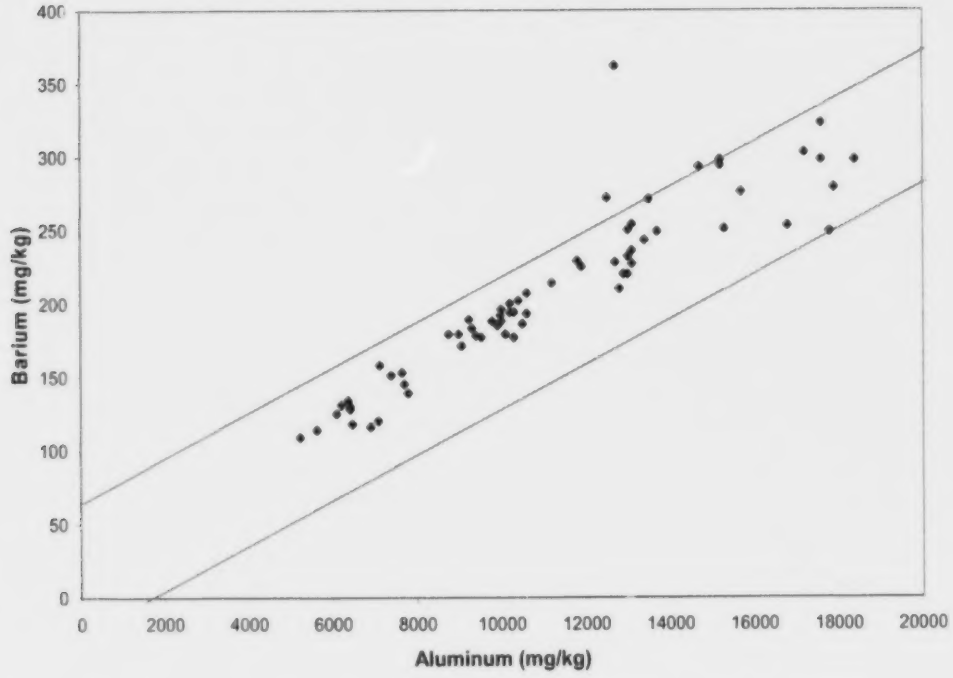

Figure 9. Barium versus aluminum for sediment cores collected on Sable Bank in 2006.

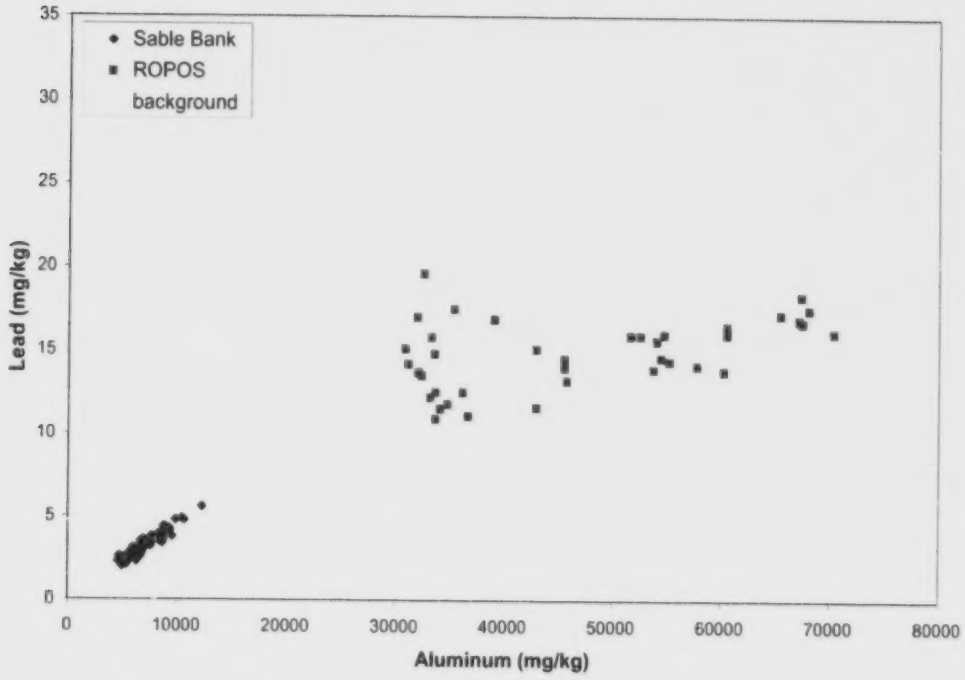

Figure 10. Lead versus aluminum for sediment cores collected in 2007.